



Initial Development of Composite Repair Resins With Low Hazardous Air Pollutant Contents

**by John J. La Scala, Scott Bingham, Kevin S. Andrews, James M. Sands, and
Giuseppe R. Palmese**

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Weapons and Materials Research Directorate, ARL**

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14. ABSTRACT <p>Unsaturated polyester-based repair resins, such as Bondo, are widely used for automotive repair, marine repair, sporting equipment repair, and household repair of metal, composites, plastics, and wood. Commercial repair resins usually contain 10 to 40 weight-percent styrene, which is a hazardous air pollutant (HAP). Reducing HAPs in Army materials has become a high priority because of Environmental Protection Agency regulations, including the Defense Land Systems for Miscellaneous Equipment National Emissions Standard for Hazardous Air Pollutants (NESHAP) and the Reinforced Plastic Composites NESHAP. Fortunately, nonvolatile fatty acid monomers can be used to replace the styrene in these repair resins. Fatty acid monomers were formulated with vinyl ester or unsaturated polyester monomers to match the glass transition temperature of commercial repair resins. Various inorganic fillers were incorporated to match the rheological and mechanical properties of commercial repair resins. These resins have zero to low HAP contents and therefore are well within emissions regulations and reduce toxicity effects on workers.</p>					
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Contents

List of Figures	iv
List of Tables	v
Acknowledgments	vi
1. Introduction	1
2. Experimental Methods	4
2.1 Repair Resin Formulation	4
2.2 Rheology and Viscosity Characterization	6
2.3 Repair Resin Cure	6
2.4 Thermogravimetric Analysis	6
2.5 Dynamic Mechanical Analysis	6
2.6 Flexural Testing	7
3. Results/Discussion	7
3.1 Rheology and Viscosity Characterization	7
3.2 Repair Resin Cure	10
3.3 Thermogravimetric Analysis	10
3.4 Dynamic Mechanical Analysis	10
3.5 Flexural Properties	17
3.6 Repair Using HAP-Free Repair Resin	17
4. Conclusions	18
5. References	19
List of Symbols, Abbreviations, and Acronyms	21
Distribution List	22

List of Figures

Figure 1. Basic formulation of environmentally friendly repair resin is a blend of UPE or VE monomers with FAMs derived from plant oils to replace styrene in commercial repair resins and inorganic fillers to make the resin into a viscous paste and reinforce the final polymer.	3
Figure 2. Viscosity as a function of shear rate for Bondo autobody filler and a HAP-free repair resin with the following composition: 19.25 weight-percent VE monomer, 35.75 weight-percent MLau (VE/MLau 35/65), 25 weight-percent talc, 15 weight-percent MgCO_3 , and 5 weight-percent glass microspheres.	8
Figure 3. Viscosity at various shear rates for HAP-free and low-HAP repair resin formulations according to table 1 relative to Bondo autobody filler.	8
Figure 4. Viscosity at various shear rates for HAP-free and low-HAP repair resin formulations containing FG relative to that of Bondo glass resin.	9
Figure 5. The viscosity of VE/MLau 35/65 measured at 1 1/s as a function of talc content.	9
Figure 6. TGA plots showing percent mass remaining vs. temperature for Bondo glass and a HAP-free resin containing 15.75 weight-percent VE monomer, 29.25 weight-percent MLau, 30 weight-percent talc, 10 weight-percent FG, and 15 weight-percent MgCO_3	11
Figure 7. Loss modulus DMA results for commercial repair resins and HAP-free repair resins with 22 weight-percent talc, 15 weight-percent MgCO_3 , and 8 weight-percent NaBO_2	11
Figure 8. Storage modulus DMA results for commercial repair resins and HAP-free repair resins with 22 weight-percent talc, 15 weight-percent MgCO_3 , and 8 weight-percent NaBO_2	12
Figure 9. Storage modulus for VE/MLau 40/60 repair resins containing 50 weight-percent binder for different fillers.	13
Figure 10. T_g for VE/MLau 40/60 repair resins containing 50 weight-percent binder.	13
Figure 11. The glassy modulus and T_g of repair resin formulations as a function of filler content (talc) in the formulation for VE/MLau 35/65.	14
Figure 12. T_g for various HAP-free formulations relative to Bondo autobody filler according to the peak of the loss modulus.	15
Figure 13. Moduli for various HAP-free formulations relative to Bondo autobody filler.	15
Figure 14. Moduli for various HAP-free formulations relative to Bondo glass.	16
Figure 15. Flexural strength and flexural modulus for Bondo glass, Bondo autobody filler, HAP-free FG (20 weight-percent VE monomer, 30 weight-percent MLau, 30 weight-percent talc, 10 weight-percent milled fiberglass, and 10 weight-percent MgCO_3), and HAP-free resin (20 weight-percent VE monomer, 30 weight-percent MLau, 30 weight-percent talc, 15 weight-percent MgCO_3 , and 5 weight-percent NaBO_2).	17
Figure 16. Photographs of HAP-free repair resin applied to dents in a truck tailgate.	18

List of Tables

Table 1. The binder formulations for the repair resins used throughout this work.	5
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Acknowledgments

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1. Introduction

Most U.S. Department of Defense weapons platforms and support equipment are subject to extremely taxing conditions and are often damaged during weapons fire and off-road operations. For many damage types, small repairs can increase the field life of the platform significantly and quickly return the weapon platform to service. Various repair resins, such as Bondo* and Belzona, are used in the field-deployed units and in U.S. Army depots (1). Repair resins contain ~20 weight-percent styrene or other hazardous air pollutants (HAPs), which are up to 50% of the resin content (2, 3). These HAP chemicals are used to reduce repair resin viscosity to allow the resin to be both easy to blend and easy to apply. Recent work has shown that HAP emissions from vehicle and marine repair are one of the largest sources of emissions. Field repair resins are always cured in the open, and it is impractical to use enclosures and trapping devices, such as scrubbers, to remove and recover these HAP emissions.

Damage to weapons platforms results from impacts from foreign objects, ballistic impacts, moisture intrusion and expansion, corrosion, collision, and various maintenance activities (4, 5). Damage levels are categorized as follows:

- Light: aesthetic repairs and coating repairs.
- Moderate: delaminations, small patches, and edge repairs.
- Heavy: full depth, core, and substructure repairs.

For a typical, moderate field repair, any remaining coating in the repair area is removed by hand sanding or portable tools. Composite repair resins, such as Bondo, containing short reinforcing fibers can then be applied to the damage zone. The resin cures at room temperature. Light repairs will be done using Bondo and similar composite repair resins without much, if any, scarfing. For most light repair and some moderate repair, Bondo and similar resins will be used. Not only are these repair resins used in composite structures, they are also used to do light and moderate repair to nonarmor metal structures, such as body paneling, by filling in holes and dents in a manner similar to that used for composite structures (6).

A recent report to the Army states that there are no environmentally friendly repair resins (7). Furthermore, through implementation of the Clean Air Act, the Environmental Protection Agency (EPA) has established regulations limiting the amount of HAPs that can be used in composite materials, including repair resins (8). This new regulation proposes facility-wide emissions limits through National Emissions Standards for Hazardous Air Pollutants (NESHAP), which makes compliance through low-emissions materials necessary or requires emissions

* Bondo is a trademark of Bondo Corp.

capture equipment (8), which is impractical for repair operations. One aspect of this law requires continuous emissions monitoring of all HAP-containing composite materials. Therefore, this legislation will have a significant impact on the use of composite materials in the military, as well as commercial applications, unless methods for mitigating HAP emissions during processing of composite parts and repairs are developed. Furthermore, the high reactivity of commercial repair chemistry results in current technology with a short shelf life (<1 year) (9). Thermal and mechanical performance characteristics decrease rapidly after expiration of the shelf life (9). Consequently, the military generates thousands of pounds of hazardous waste from expired resins annually (6, 9).

The U.S. Army Research Laboratory (ARL) in conjunction with Drexel University has recently shown that fatty acid monomers (FAMs) are ideal candidates to replace styrene in vinyl ester (VE) and unsaturated polyester (UPE) resins because they are inexpensive, have low volatilities, and promote global sustainability because they are derived from renewable resources: plant oils (10–12). Triglycerides are the main component of oils derived from plant and animal sources and are composed of three fatty acids connected by a glycerol center (13). Triglycerides are simply broken down into fatty acids using industrial processes, such as acidolysis (14). A number of synthetic routes have been established by ARL/Drexel for making fatty acid-based monomers (10). The methacrylated fatty acid (MFA) monomer (figure 1) has proven to be the best FAM for composite production. MFA monomers are produced through a simple addition reaction of the carboxylic acid of fatty acids with the epoxide group of glycidyl methacrylate to form a single product within a few hours at reaction temperatures ranging from room temperature to 80 °C (10). Each MFA contains one terminal polymerizable unsaturation site per molecule. In this way, the FAMs act as chain extenders, analogous to styrene in VE/UPE resins. The resulting monomers have fairly high molecular weight and are nonvolatile, making them excellent alternatives to styrene in liquid-molding resins. Furthermore, these monomers promote global sustainability because they are made using a renewable resource. Due to the low cost of fatty acids and the simple modifications to produce FAMs, these monomers are inexpensive, with an estimated cost only slightly above that of styrene. Although plant oils have been used to make polymers for years, using FAMs as reactive diluents is a novel concept (10).

Repair resins are usually two-part formulations composed of a number of different components. Part A contains the polymeric binder, including a cross-linking agent (e.g., VE or UPE monomers) and a reactive diluent (e.g., styrene), free-radical decomposition promoter, free-radical inhibitors, and various inorganic additives, such as talc, magnesium carbonate (MgCO_3), chopped glass fiber, sodium metaborate (NaBO_2), and fumed silica (2, 3). Part B contains the free-radical initiator and surfactants to enable successful mixing of this hardener into a viscous part A (15) and is typically added to part A in amounts of 5 weight-percent or less.

The filler content in commercial repair resins is typically 45–55 weight-percent of the resin, while the resin binder makes up the remaining 55–45 weight-percent (2). The organic resin is

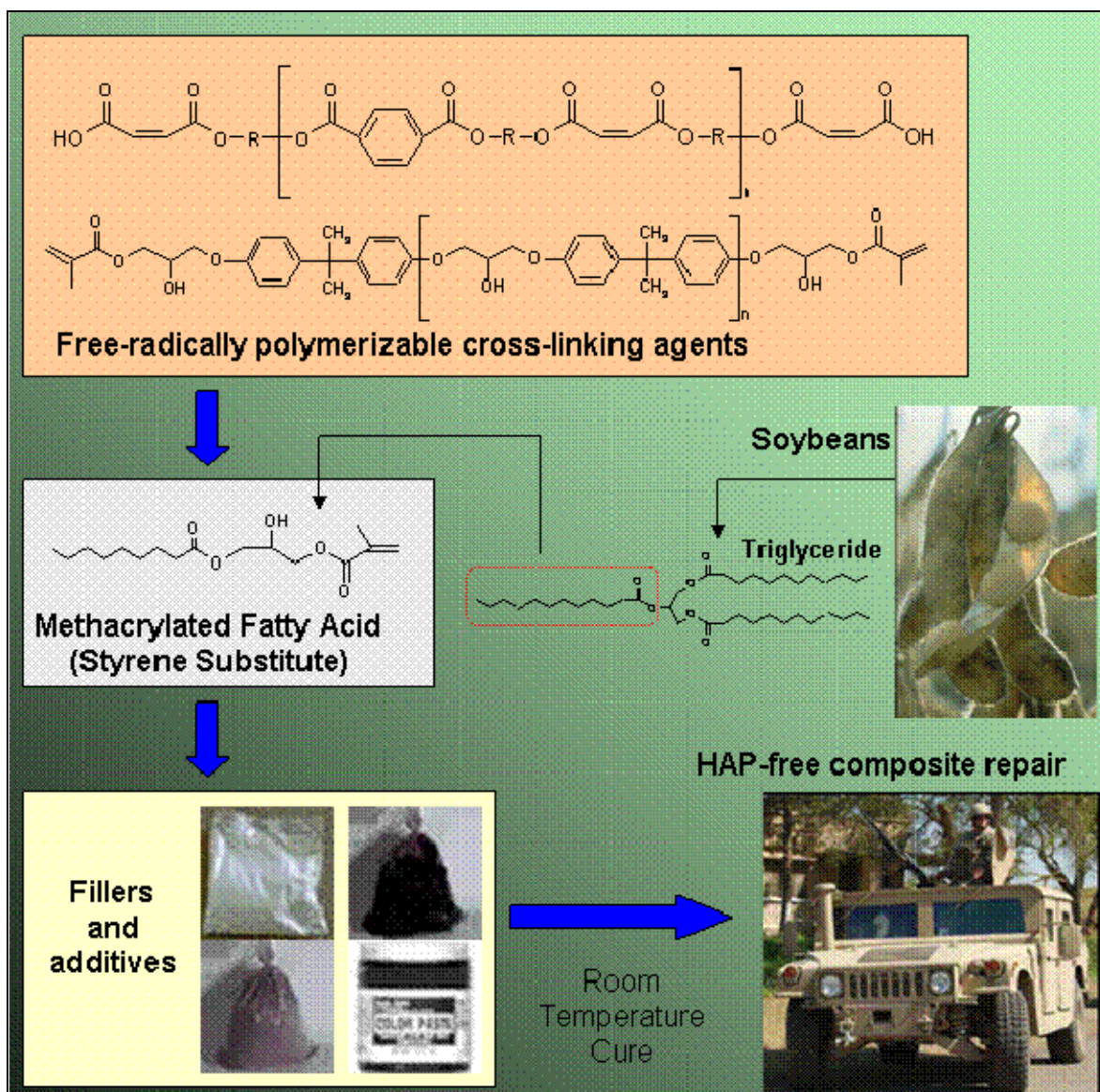


Figure 1. Basic formulation of environmentally friendly repair resin is a blend of UPE or VE monomers with FAMs derived from plant oils to replace styrene in commercial repair resins and inorganic fillers to make the resin into a viscous paste and reinforce the final polymer.

typically composed of UPE monomers and styrene. The UPE monomers are composed of diethylene glycol units combined with phthalic acid units, which impart stiffness, and maleic acid or fumaric acid units, which contain the vinyl functionality enabling free-radical polymerization (2, 16, 17). The styrene content in Bondo repair resins ranges from 14 to 17 weight-percent based on the total resin content or 27–31 weight-percent based on the organic resin part (2, 3). The inorganic additives typically used in these resins are talc, magnesium carbonate, glass microspheres, glass fibers, and sodium metaborate (2, 3). Glass-reinforced resins, such as Bondo glass, contain ~5 weight-percent fiberglass (FG) (3), which produces a

strong rigidizing effect relative to other additives. Lower-grade repair resins use ~3–5 weight-percent glass microspheres (2) instead of FG to reduce density and resin viscosity. Sodium metaborate is used for a temporal effect on viscosity during processing. The viscosity remains low but increases with time after initial processing. As such, small amounts of sodium metaborate (~2 weight-percent [2]) are used to allow for low viscosities during processing but form higher viscosities during shipment and storage, giving the proper viscosity and consistency for repair applications. Benzoyl peroxide is typically used as the initiator in repair resin putties, though methyl ethyl ketone peroxide is typically used to cure unfilled resins (2, 3, 16). N,N-Dimethylaniline is typically added to the base Bondo resin (component A) and acts as a promoter to break down the benzoyl peroxide and allow for free radical polymerization at room temperature. N,N-Dimethylaniline is used in amounts of ~0.25% by weight of the repair resin.

This work presents a method to use MFA monomers to partly or completely eliminate styrene in repair resins. The FAMs were blended with VE and UPE resins and various filler to create low-HAP and HAP-free repair resin putties with similar properties relative to commercial repair resins. A patent application has been filed for these HAP-free and low-HAP repair resin formulations (18).

2. Experimental Methods

2.1 Repair Resin Formulation

Commercially available repair resins, Bondo autobody filler and Bondo glass, were used in this work as a point of comparison. Both of these resins have similar constituents according the literature (2, 3). The one main difference between these resins is that Bondo glass is formulated with FG filler particles, whereas Bondo autobody filler does not contain any FG.

Zero HAP and low-HAP environmentally friendly repair resin binders were formulated by blending FAMs with VE and UPE monomers (figure 1). Various compositions of VE/UPE and MFA monomers (Applied Poleramics Inc., Benecia, CA) were used to make a variety of repair resin formulations (table 1). In particular, methacrylated octanoic acid (MOct) and methacrylated lauric acid (MLau) were used to formulate many of the HAP-free repair resins because of their good properties in composite resins and their ability to be easily produced at large scales.

VE repair formulations were prepared using a commercial VE, CN-151 (Sartomer, Exton, PA), as the cross-linker (19). MLau in quantities ranging from 35–80 weight-percent was added into the VE formulation and blended by heating and mechanical mixing. Styrene was used in some VE repair resin formulations to make low-HAP, rather than HAP-free, formulations. To a blend containing 35 weight-percent CN-151 and 65 weight-percent MLau, styrene was added to the resin in the amount of 10 weight-percent by manually stirring at room temperature.

Table 1. The binder formulations for the repair resins used throughout this work.

Monomer	Binder Formulation Number					
	1 (Weight-Percent)	2 (Weight-Percent)	3 (Weight-Percent)	4 (Weight-Percent)	5 (Weight-Percent)	6 (Weight-Percent)
VE (CN-151)	30	35	40	31.5	—	—
UPE (Bondo autobody resin)	—	—	—	—	50	—
UPE (Bondo FG resin)	—	—	—	—	—	55
MLau	70	65	60	58.5	—	—
MOct	—	—	—	—	45	35
Styrene	—	—	—	10	5	10

UPE monomers from Bondo FG resin (20) were also used in separate formulations as cross-linkers (table 1). MLau was not soluble in the UPE monomers tested. On the other hand, MOct was soluble because of its shorter fatty acid chain length and was used in all UPE formulations. In one set of samples, Bondo UPE from Bondo autobody filler was purified from the fillers by dissolving about 18 g of repair resin in about 25 g of acetone in 50-mL centrifuge tubes. The organic phase readily dissolved in the acetone, while the inorganic fillers settled to the bottom of the tube. The organic components dissolved in the acetone were recovered and allowed to evaporate in the ambient environment for 1 week. The resin was then placed in an oven at 50 °C for 1 week to remove the acetone and styrene. After evaporation, ~4–5 weight-percent styrene and <1 weight-percent acetone remained. A blend of 55 weight-percent of this UPE (containing ~5 weight-percent styrene and acetone) and 45 weight-percent MOct was then prepared. In another set of samples, 57.51 g of Bondo FG resin containing 28 weight-percent styrene was blended with 15.93 g of MOct. The resin was allowed to evaporate for 2 weeks at room temperature until 12.33 g of styrene evaporated from the resin. Then 2.6 g of styrene was added back to the resin to produce a resin with 55 weight-percent UPE monomer, 35 weight-percent MOct, and 10 weight-percent styrene.

N,N-dimethylaniline (Sigma-Aldrich) was added to the part A formulation because this chemical promotes free radical cure of benzoyl peroxide initiators, which are typically used in the hardener component. N,N-dimethylaniline content in the amount of 0.1–0.5 weight-percent worked best for adequately curing the repair resin and allowing sufficient working time. Inorganic components, including talcum (Fisher Scientific, laboratory grade), milled glass fibers (Jamestown Distributors), magnesium carbonate penta-hydrate ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$, Fisher Scientific), sodium metaborate hydrate (NaBO_2 , MP Biomedical), aluminum oxide (Alodur), sand, silica thickener (Jamestown Distributors), glass microspheres (3M Scotchbrite K37), and phenolic microballoons (Jamestown Distributors) were thoroughly mixed into the resin formulations using high shear mixers. Silica thickener, sand, phenolic microballoons, aluminum oxide, and carbon black were only tested qualitatively in this manner because they are not commonly used in repair resins (2, 3). Various inorganic components and contents with various particle sizes were used.

Overall, all of these fillers acted similarly in increasing the viscosity of the uncured resin and increasing the stiffness of the cured polymer. The following abbreviations are used for talc (T), magnesium carbonate (M), sodium metaborate (N), glass microspheres (MS), and milled FG.

2.2 Rheology and Viscosity Characterization

The viscosities of the uncured resin samples were measured using a TA Instruments (New Castle, DE) AR2000 rheometer in steady shear flow experiments using parallel plate geometry (40-mm plates). The shear rate was increased from 0.001 to 10 s⁻¹ and then decreased back to 0.001 s⁻¹, and 10 measurements were taken per decade. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive intervals.

2.3 Repair Resin Cure

The repair resin was cured using the Bondo red cream hardener. The hardener in the amount of 1% by weight was thoroughly mixed into the resin, until the resin was a uniform pink color. The resins were then added to silicon rubber molds using a spatula. The resins were allowed to cure overnight. The cured polymer samples were removed from the mold and then cut into the appropriate sizes for testing. All samples were sanded to remove any surface defects and to ensure the surfaces were flat.

2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was run on the samples using a TA Instruments hi-res TGA 2950. A 10-mg sample was placed on a platinum sample holder. The samples were run in air up to 800 °C at 10 °C/min. The instrument measures the sample mass as a function of temperature throughout the experiment. Liquid component A and liquid red cream hardener (component B) were run. In addition, cured samples were also run.

2.5 Dynamic Mechanical Analysis

The thermomechanical properties of the repair resins were measured using dynamic mechanical analysis (DMA). Rectangular samples with approximate dimensions of 25 × 9 × 3 mm were tested using a TA Instruments 2980 DMA in single cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 μm while ramping the temperature from -50 to 150 °C at a rate of 2 °C/min. Two temperature ramp experiments were run for each sample. The two ramps were nearly identical, indicating almost complete cure after the first run and indicating that additional DMA ramps were unnecessary.

The temperature at which the peak in the loss modulus occurred in the fully post-cured polymer was considered the glass transition temperature of the material (21). The experimental error in T_g (glass transition temperature) was ±1.5 °C. Tan(δ) can also be used as a measure of the glass transition temperature, but it is known that the maximum in tan(δ) is 10–20 °C above the loss

modulus maximum. The loss modulus peak represents the midpoint of the T_g , while $\tan(\delta)$ represents the end of the glass transition region and subsequent beginning of the rubbery region. Because both of these can be independently affected by the formulation, both of these values were recorded for each formulation.

2.6 Flexural Testing

Flexural tests, in accordance with ASTM D 790-92 (22), were performed to determine the modulus of elasticity and flexural strength. The samples had approximate dimensions of $10 \times 80 \times 64$ mm and actual dimensions were measured prior to testing. The samples were tested flatwise on a support span, resulting in a support-to-depth ratio of 16. All tests were performed at ambient conditions, which were ~ 22 °C and 40% relative humidity. The samples were tested using an Instron at a crosshead speed of 10 mm/min. The flexural modulus, elongation at failure, and flexural strength were calculated according to the ASTM standard.

3. Results/Discussion

3.1 Rheology and Viscosity Characterization

Repair resins must have sufficient viscosities so that they stick to the repair area and do not spread too thin. In many cases, repair resins must stick to an upside-down surface. On the other hand, the resin must have a low enough viscosity that it can be removed from the container at room temperature and be hand mixed with the hardener component. Therefore, an attempt was made to match the viscosity of HAP-free FAM binders with those of commercial binders. However, this was difficult because the viscosity of styrene (1 cP) is much lower than the viscosity of MLau (~ 60 – 70 cP). Furthermore, commercial resins shear thin and, as such, have viscosities that vary according to the shear rate applied (figure 2). Yet, it was possible to match the rheology of the HAP-free formulations to that of commercial repair resins (figure 2). Not only do the Newtonian viscosities match (i.e., the region where viscosity is not a function of shear rate), but both resins shear thin at similar shear rates and have similar power-law relationships in the non-Newtonian regime. In general, repair resins were prepared with a variety of viscosities, ranging from lower to higher viscosities relative to their commercial counterparts (figures 3 and 4). Note that the resins containing FG (figure 4) had higher viscosities relative to resins without FG (figure 3). Overall, resin viscosity was dominated by resin/filler ratio; the larger the filler content, the higher the viscosity (figure 5). Furthermore, as the styrene and MLau content increased, the resin viscosity decreased. Therefore, repair resins can be created with the necessary rheological properties for typical repair scenarios.

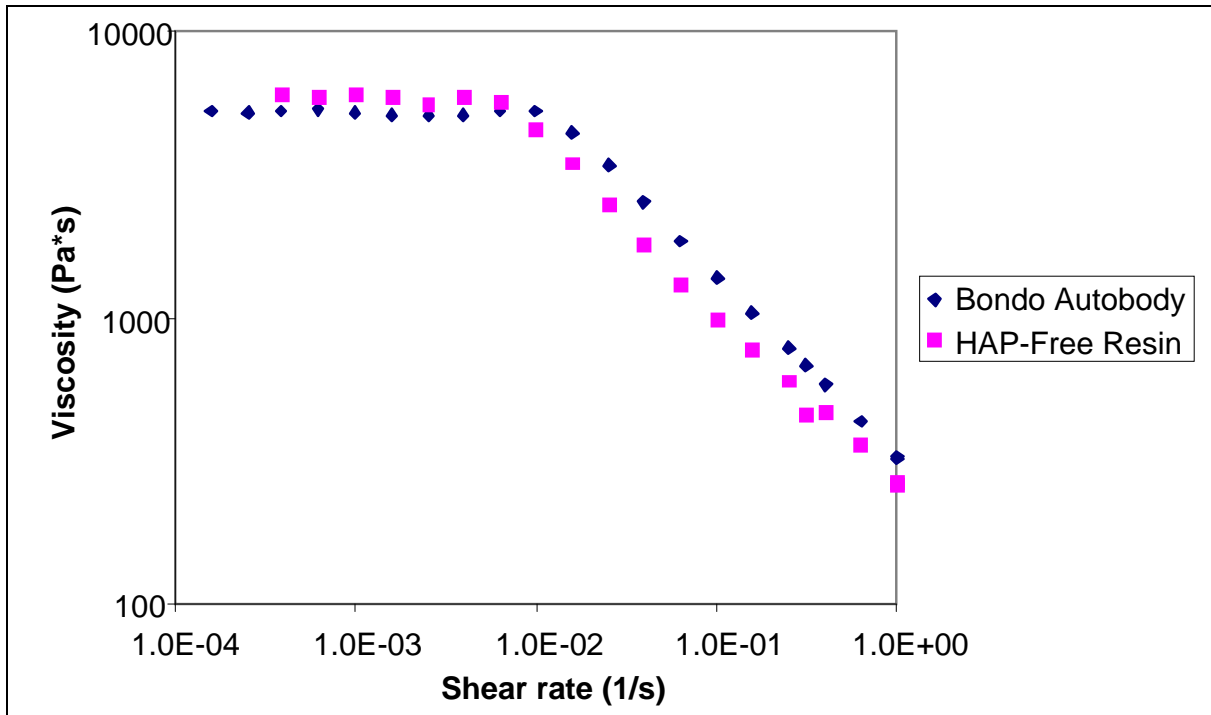


Figure 2. Viscosity as a function of shear rate for Bondo autobody filler and a HAP-free repair resin with the following composition: 19.25 weight-percent VE monomer, 35.75 weight-percent MLau (VE/MLau 35/65), 25 weight-percent talc, 15 weight-percent MgCO_3 , and 5 weight-percent glass microspheres.

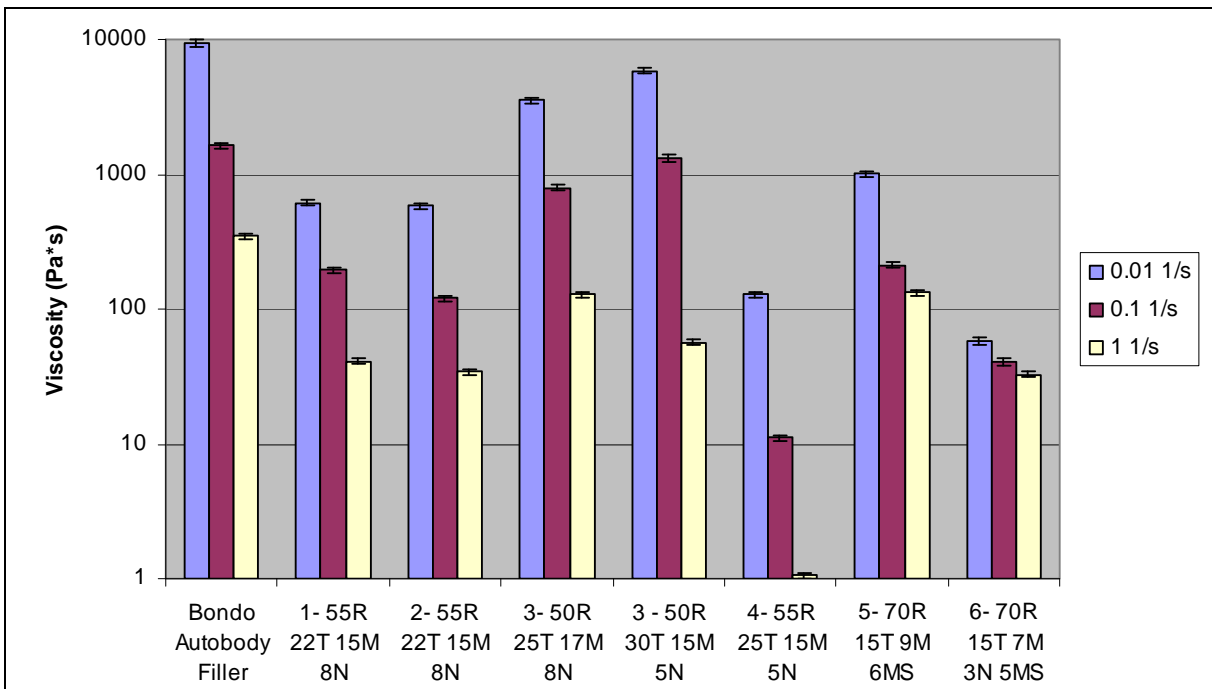


Figure 3. Viscosity at various shear rates for HAP-free and low-HAP repair resin formulations according to table 1 relative to Bondo autobody filler.

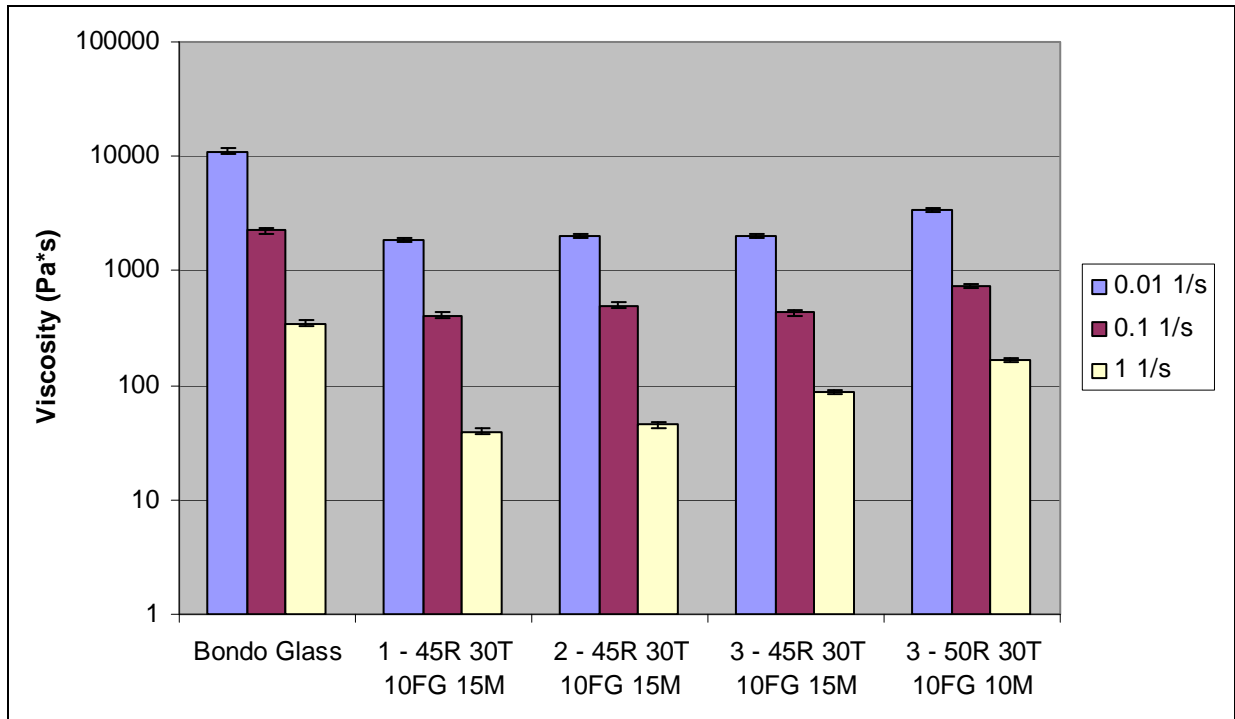


Figure 4. Viscosity at various shear rates for HAP-free and low-HAP repair resin formulations containing FG relative to that of Bondo glass resin.

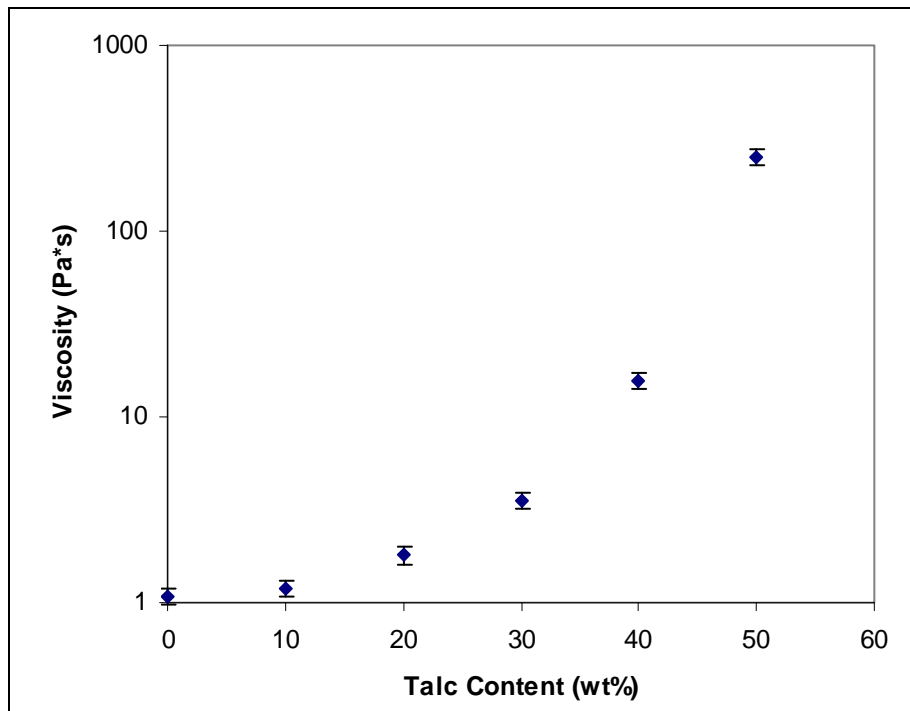


Figure 5. The viscosity of VE/MLau 35/65 measured at 1 1/s as a function of talc content.

3.2 Repair Resin Cure

Bondo resins and fatty acid-based repair resins cured similarly. If short working times are desired, adding 5 weight-percent Bondo red cream hardener caused curing to occur within 5 min, while 1 weight-percent red cream hardener caused curing within 30 min, allowing for longer working times.

To avoid using commercially formulated hardeners, benzoyl peroxide was mixed with other oils and surfactants. One hardener for the repair resin was formulated by blending benzoyl peroxide (30 weight-percent) with Gojo Multi Green hand cleaner (70 weight-percent). Another hardener was formulated by blending benzoyl peroxide (30 weight-percent), Gojo Multi Green hand cleaner (50 weight-percent), and canola oil (20 weight-percent) together. These formulated hardeners were mixed thoroughly with the resin. The high-surfactant contents of the hardener allowed for easy blending with the viscous repair resin. The resulting resin gelled in a few minutes and cured into a hard but flexible solid. This shows that simple hardeners can be easily prepared. These formulated hardeners were used for proof of concept purposes and not used to formulate any samples for testing (DMA, Instron, etc.) in this work.

3.3 Thermogravimetric Analysis

TGA was run on commercial and zero-HAP formulated repair resins (figure 6). For the HAP-free resins, less mass loss occurred at lower temperatures due to the nonvolatile nature of the FAMs vs. the highly volatile styrene in Bondo. Overall, the commercial and zero-HAP resins lose approximately the same amount of mass as resins with similar binder contents. For resins with greater filler contents, the final char weight was higher.

3.4 Dynamic Mechanical Analysis

Figure 7 shows the loss moduli and figure 8 shows the storage moduli for various formulations as a function of temperature. Bondo autobody filler, Bondo glass, and Bondo all-purpose putty all had glass transition temperatures of 20–25 °C. VE/MLau ratios of 20/80 matched the T_g and glassy modulus of commercial repair resins (figures 7 and 8). Resins with VE/Lau ratios of 35/65 had higher T_g 's than that of commercial resins but had similar room temperature moduli (figure 7). However, the glass transition was significantly broader for the fatty acid-based repair resin (figure 7). This broader T_g prevents the HAP-free repair resins from having identical DMA properties as a function of temperature. On the other hand, the broader T_g allows the resin more flexibility so it is less fragile in cold weather. UPE/MOOct/Sty 50/45/5 also produced similar DMA properties relative to commercial repair resins.

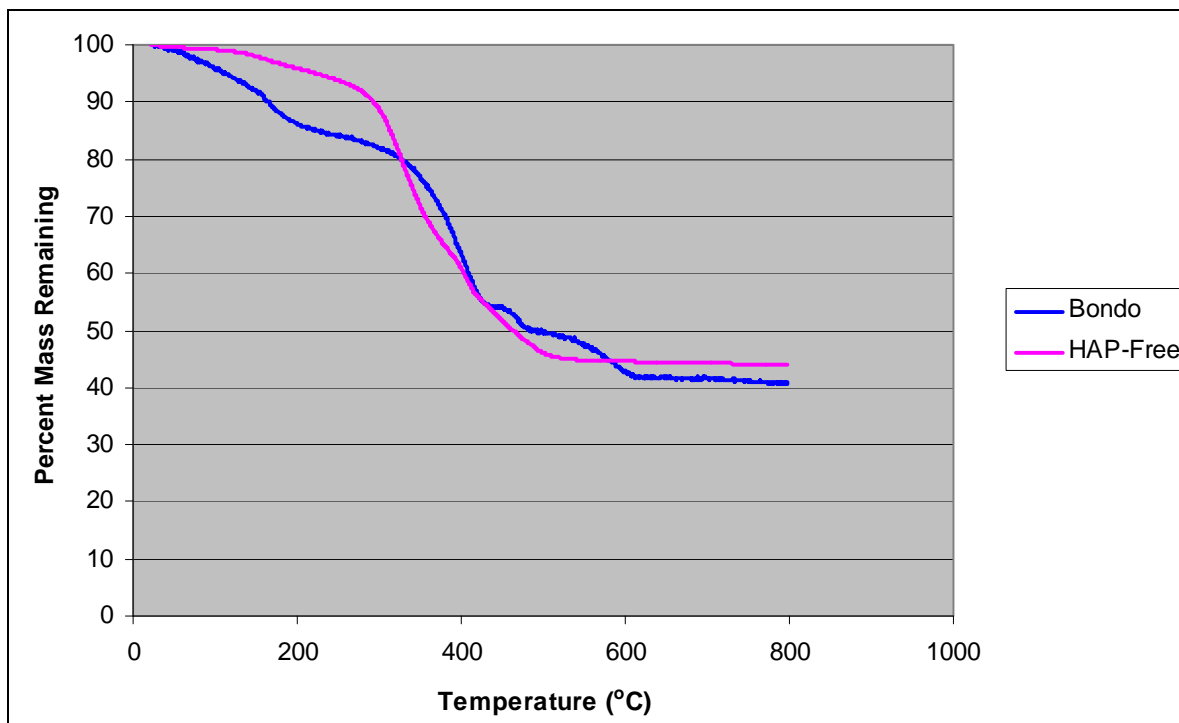


Figure 6. TGA plots showing percent mass remaining vs. temperature for Bondo glass and a HAP-free resin containing 15.75 weight-percent VE monomer, 29.25 weight-percent MLau, 30 weight-percent talc, 10 weight-percent FG, and 15 weight-percent MgCO_3 .

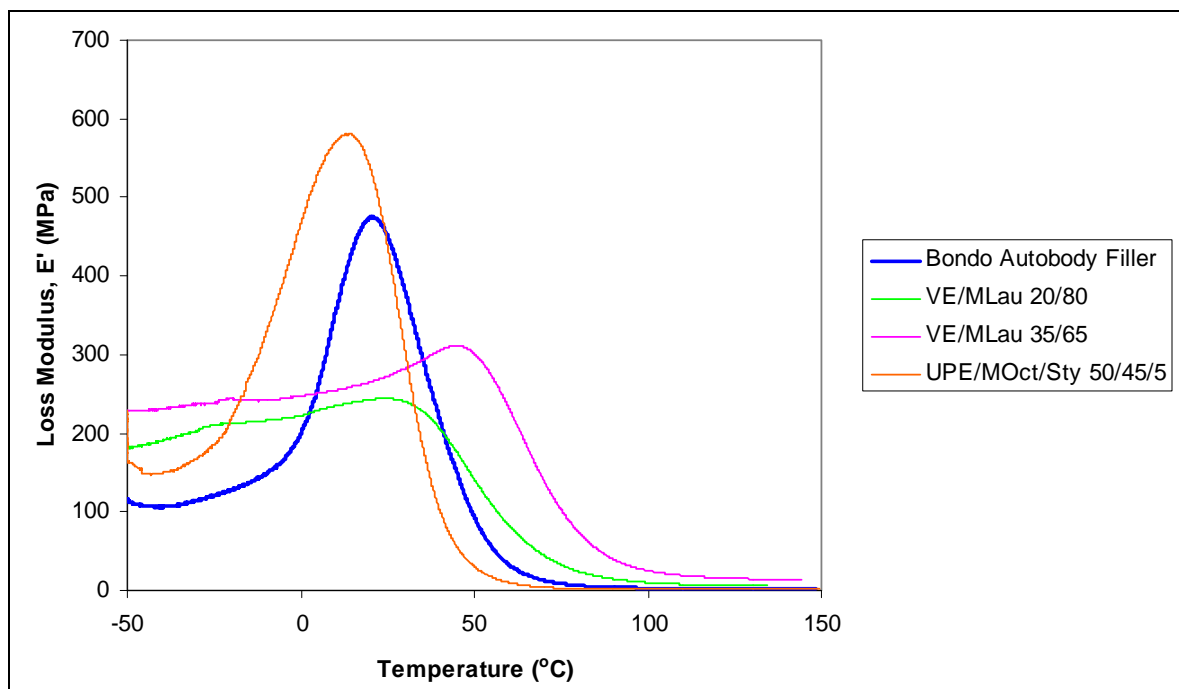


Figure 7. Loss modulus DMA results for commercial repair resins and HAP-free repair resins with 22 weight-percent talc, 15 weight-percent MgCO_3 , and 8 weight-percent NaBO_2 .

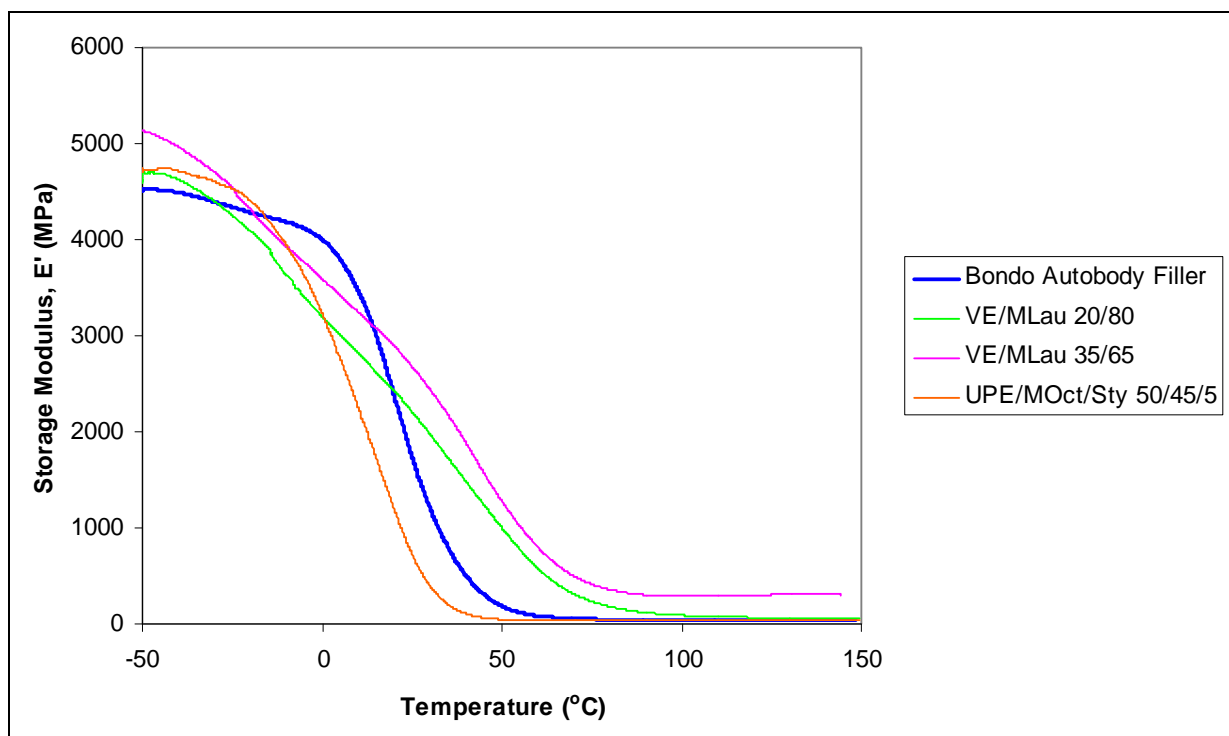


Figure 8. Storage modulus DMA results for commercial repair resins and HAP-free repair resins with 22 weight-percent talc, 15 weight-percent MgCO_3 , and 8 weight-percent NaBO_2 .

Figure 9 shows the glassy and room-temperature moduli, and figure 10 shows the T_g for the same binder formulation (VE/MLau 40/60) and the same binder content (50 weight-percent) but with varying amounts of talc, magnesium carbonate, and sodium metaborate. The results clearly show that at this binder content, the particular fillers used have little effect on modulus and T_g . Note that none of the resins in figure 10 used FG as filler. Similarly, figure 11 shows that increasing the resin binder content has no significant effect on T_g for the polymer in the range of 45–75 weight-percent binder. From 90 weight-percent to 100 weight-percent binder content, the T_g decreased by as much as 5 °C as a result of reduced stiffening. Note that the loss modulus trends and $\tan(\delta)$ trends do not match exactly. Because the loss modulus represents the midpoint of the glass transition, while $\tan(\delta)$ represents a maximum in viscous to elastic response, the loss modulus maximum is more typically used to represent T_g and is used as such throughout the rest of this work. On the other hand, the glassy modulus increased as the filler content increased (figure 11). This is expected because the fillers should be capable of carrying a load across the sample once percolation of the filler particles occurs. Load-bearing capacity and stiffness should increase as the concentration of particles increases above the percolation threshold (23). These results show that filler content alone affects the modulus, and the individual fillers used are of little importance.

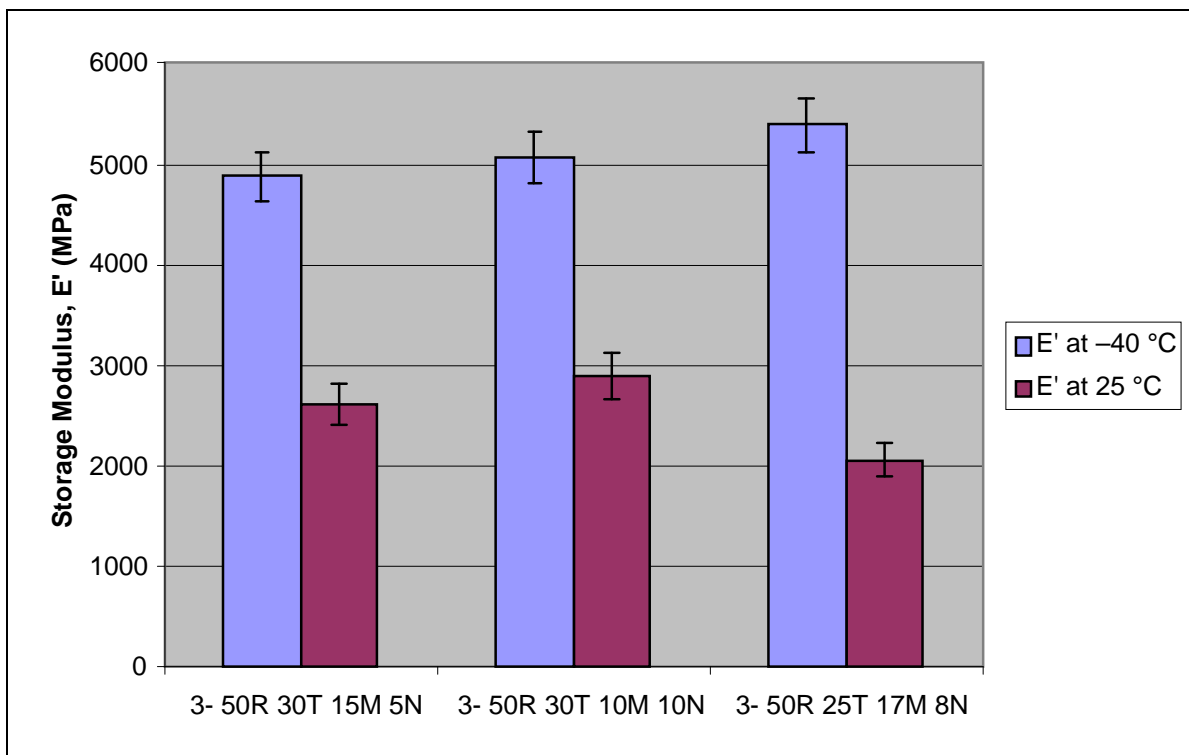


Figure 9. Storage modulus for VE/MLau 40/60 repair resins containing 50 weight-percent binder for different fillers.

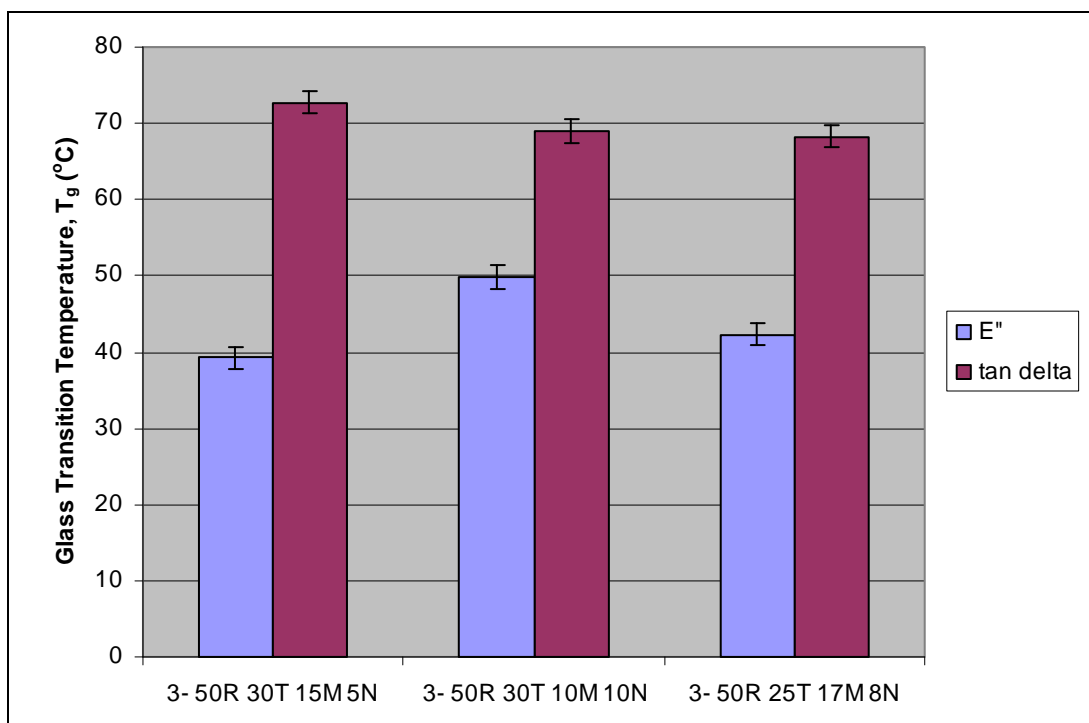


Figure 10. T_g for VE/MLau 40/60 repair resins containing 50 weight-percent binder.

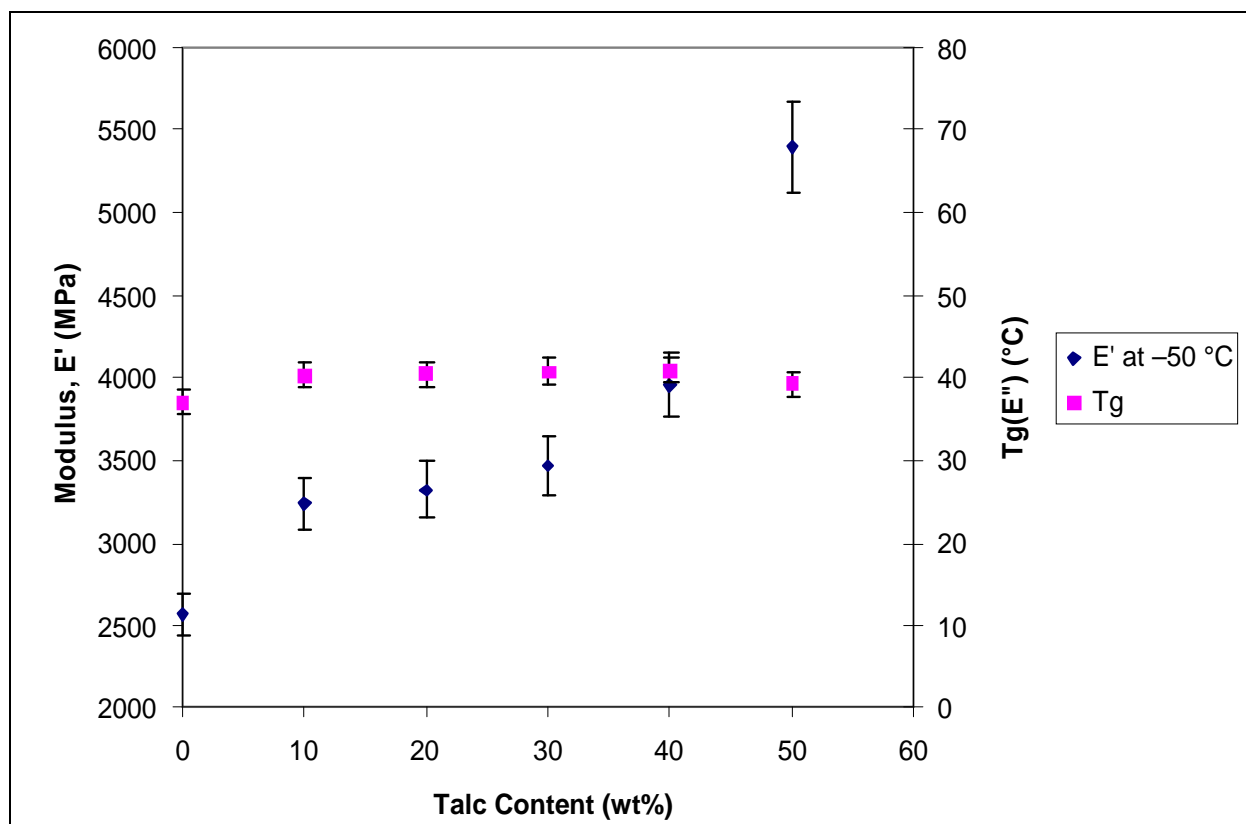


Figure 11. The glassy modulus and T_g of repair resin formulations as a function of filler content (talc) in the formulation for VE/MLau 35/65.

Figures 12 and 13 show the properties of each resin formulation (table 1) with selected amounts and ratios of fillers. Overall, similar dynamic mechanical properties relative to commercial resins were achievable with selected resin formulations. In addition, depending on need, resin T_g 's can be selected with similar, higher, or lower values relative to commercial repair resins (figure 12). As expected, T_g increased as the VE content in VE/MLau formulations increased from 30% (binder formulation 1) to 40% (binder formulation 3). In addition, T_g further increased according to the loss modulus for the VE/MLau sample with 10% styrene (binder formulation 4) because polystyrene has a higher T_g relative to poly-MLau (11). All the VE/MLau formulations shown had T_g values above that of the commercial repair resin. Yet, the T_g of the repair resin could be dropped by simply increasing the MLau-to-VE ratio (11). The UPE resin formulations had slightly lower T_g 's than the commercial repair resin. This is again a result of the low T_g of poly-MOOct relative to polystyrene. Increasing the styrene content from 5 weight-percent (binder formulation 5) to 10 weight-percent (binder formulation 6) increased T_g significantly. Yet, the purpose is to develop styrene-free repair resins. To do this and prepare resins with similar T_g relative to the commercial resins, either a higher T_g UPE monomer must be used as a partial or complete replacement for the Bondo UPE or a higher T_g nonvolatile

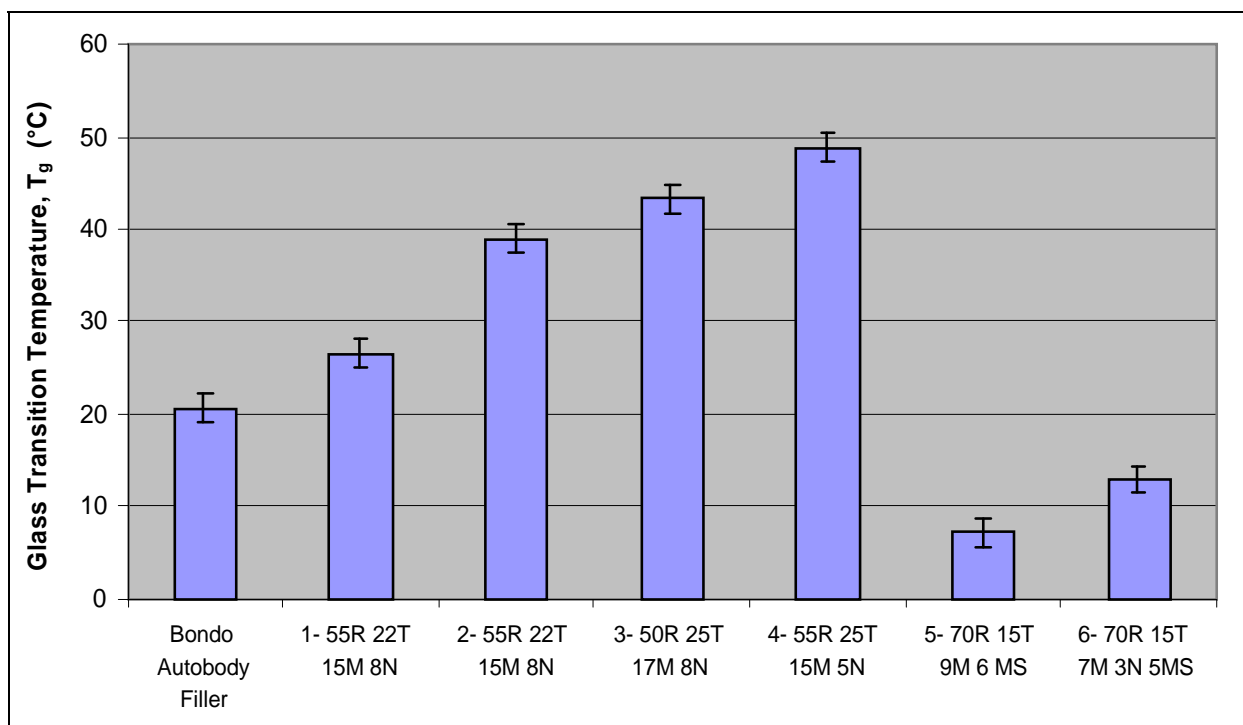


Figure 12. T_g for various HAP-free formulations relative to Bondo autobody filler according to the peak of the loss modulus.

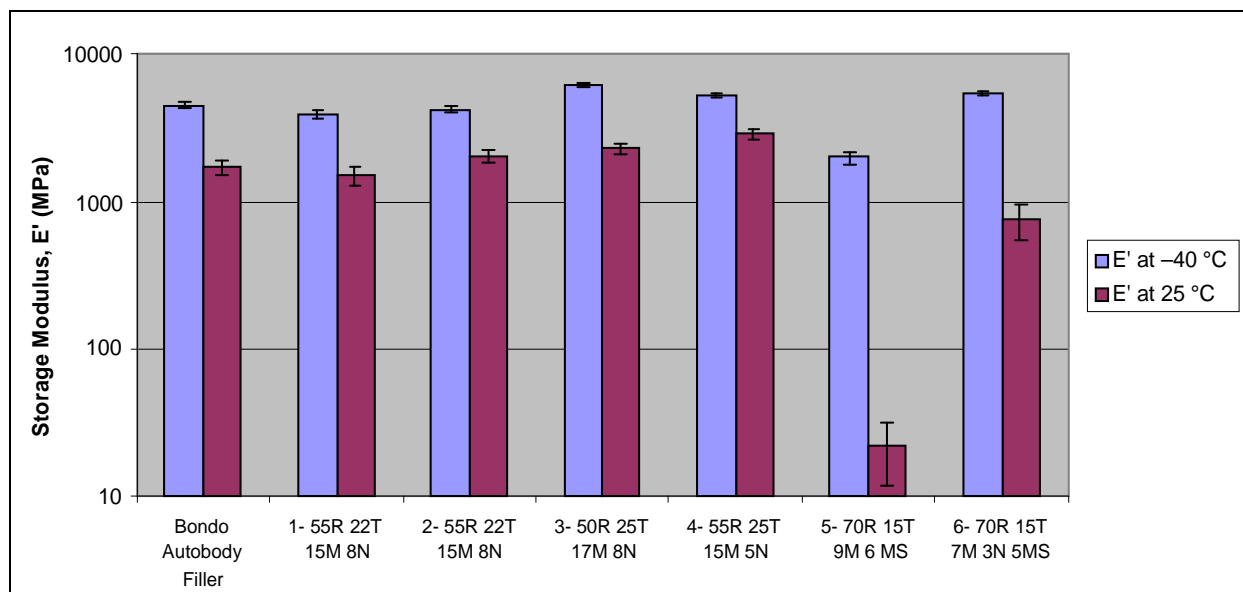


Figure 13. Moduli for various HAP-free formulations relative to Bondo autobody filler.

monomer must be used as a partial or complete replacement for styrene and MOct. Figure 13 shows that despite these changes in T_g , there is little effect on the mechanical performance of these resins, with the exception of the UPE/MLau/Sty 50/45/5 (binder formulation 5). However, this repair resin was also formulated with the lowest content of fillers, which is a contributing effect for this reduced modulus. Figure 14 shows the mechanical properties of repair resins formulated with FG. The glassy modulus is considerably higher for these formulations relative to resins without FG (figure 13). Thus high aspect ratio solid fillers like FG do affect mechanical properties to a larger degree than particle fillers, like talc and magnesium carbonate. However, the room temperature modulus and T_g are not significantly affected by adding FG because T_g is a resin-dominated phenomenon and room temperature is very close to T_g so that filler-type effects are being masked by drastic changes in resin stiffness. Overall, similar dynamic mechanical properties relative to commercial resins were achievable. Also, lower and higher T_g 's and moduli were easily formulated by varying the FAM content and filler contents in the resin.

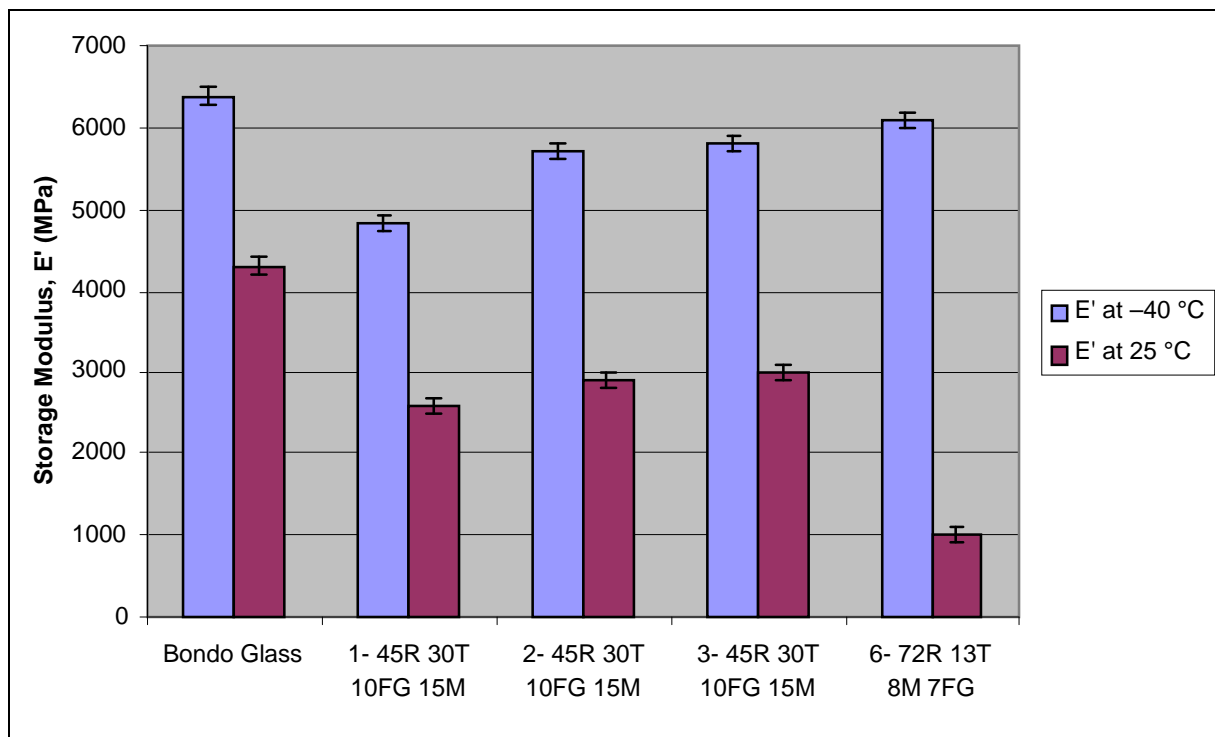


Figure 14. Moduli for various HAP-free formulations relative to Bondo glass.

3.5 Flexural Properties

The samples using FG had significantly higher moduli and strengths than the samples without FG (figure 15). However, there was no significant difference between the properties of commercial resins using FG and HAP-free formulated resins with FG. There was also no significant difference in the properties of the Bondo autobody filler and the HAP-free formulation using talc, MgCO_3 , and NaBO_2 as fillers.

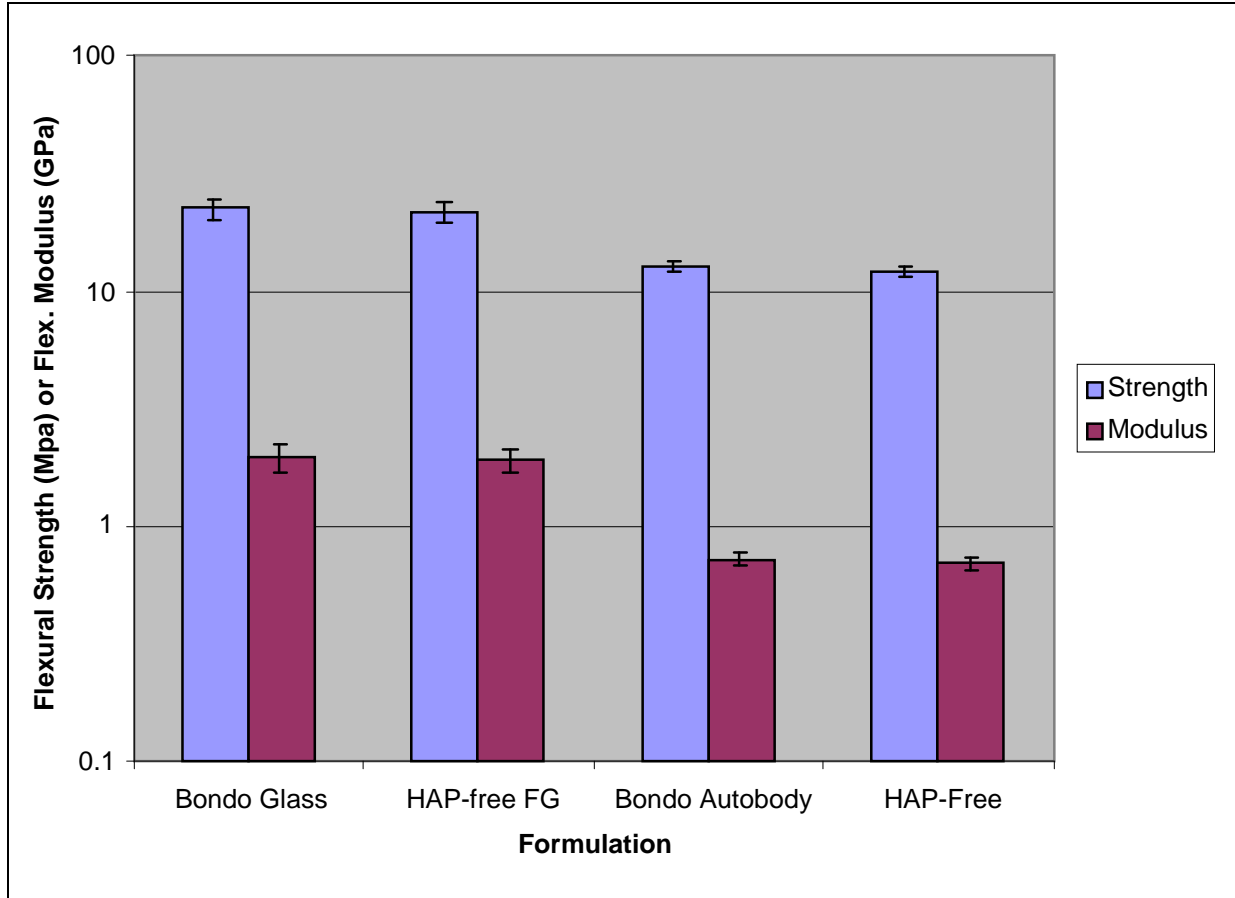


Figure 15. Flexural strength and flexural modulus for Bondo glass, Bondo autobody filler, HAP-free FG (20 weight-percent VE monomer, 30 weight-percent MLau, 30 weight-percent talc, 10 weight-percent milled fiberglass, and 10 weight-percent MgCO_3), and HAP-free resin (20 weight-percent VE monomer, 30 weight-percent MLau, 30 weight-percent talc, 15 weight-percent MgCO_3 , and 5 weight-percent NaBO_2).

3.6 Repair Using HAP-Free Repair Resin

A dented truck tailgate was repaired using a zero-HAP repair resin formulation. This formulation had 19.25 weight-percent CN-151, 35.75 weight-percent MLau, 22 weight-percent talc, 17 weight-percent MgCO_3 , and 8 weight-percent NaBO_2 . The application of the resin and

cure was similar to that of commercial repair resins. The resulting repair was excellent as shown in figure 16. The product was able to be sanded down to produce a smooth surface similar to that of commercial repair resins. Scraping the edges of the repaired area with a razor blade did not result in delamination of the resin. This shows that the repair resin had good adhesion properties with the substrate.



Figure 16. Photographs of HAP-free repair resin applied to dents in a truck tailgate.

4. Conclusions

This work clearly shows that HAP-free repair resins based on VEs, UPEs, and MFAs were formulated. These resins contain no styrene, unlike commercial repair resins that contain 14–17 weight-percent styrene. As a result, these repair resins exceed the Reinforced Plastic Composites NESHAP regulations and meet the Defense Land Systems for Miscellaneous Equipment NESHAP regulations. These HAP-free resins had similar rheological, thermal, and mechanical properties relative to commercially available repair resins, like Bondo. As a result, using these HAP-free repair resins should result in high-quality repair and allow environmentally compliant repair of vehicles while eliminating worker exposure to harmful emissions. Yet additional work needs to be done to optimize the properties of these repair resins for a variety of applications.

5. References

1. Misc. Adhesives and Sealants Technology Thrust Area. Concurrent Technologies Corporation, Potential Alternatives Report (CDRL A007) Task No. 0420, December 2005.
2. Bondo Corporation. Bondo Body Filler Materials Safety Data Sheet, Atlanta, GA, June 2006.
3. Bondo Corporation. Bondo Glass Reinforced Filler Materials Safety Data Sheet, Atlanta, GA, March 2001.
4. Mehkam, P. Support of Composite Structures on Naval Aircraft. Presented at Second Joint NASA/FAA/DOD Conference on Aging Aircraft, Williamsburg, VA, 1998.
5. Koon, R. W. Aircraft Skin Repair Procedures and Requirements. Invited presentation at U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1998.
6. Fink, B. K.; McKnight, S. H.; Newton, C. H.; Gillespie, J. W.; Palmese, G. R. *Non-Polluting Composites Repair and Remanufacturing for Military Applications: An Environmental and Cost-Savings Analysis*; ARL-TR-2139; U.S. Army Research Laboratory: Aberdeen Proving Ground, MD, December 1999.
7. Misc. Adhesives and Sealants Technology Thrust Area. Concurrent Technologies Corporation, Gap Analysis Report (CDRL A007) Task No. 0420, February 2006.
8. Environmental Protection Agency. National Emissions Standards for Hazardous Air Pollutants: Reinforced Plastic Composites Production. *Federal Register* **2003**, 68, 19375.
9. Sands, J. M.; Fink, B. K.; McKnight, S. H.; Newton, C. H.; Gillespie, J. W.; Palmese, G. R. *Clean Products and Processing* **2001**, 2, 228–235.
10. Palmese, G. R.; La Scala, J. J.; Sands, J. M. Fatty Acid Monomers to Reduce Emissions and Toughen Polymers. U.S. Patent Appl. 60/569,379, May 2005.
11. La Scala, J. J.; Sands, J. M.; Orlicki, J. A.; Robinette, E. J.; Palmese, G. R. Fatty Acid-Based Monomers as Styrene Replacements for Liquid Molding Resins. *Polymer* **2004**, 45, 7729–7737.
12. La Scala, J. J.; Sands, J. M.; Palmese, G. R. Clearing the Air: Army Composites Research Reduces Harmful Emissions. *The AMPTIAC Quarterly* **2004**, 8, 118–125.
13. Litchfield, C. *Analysis of Triglycerides*; Academic Press: New York, 1972; p 3.
14. Gunstone, F. D. *Fatty Acid and Lipid Chemistry*; Blackie Academic and Professional: New York, 1996; p 72.

15. Bondo Corporation. Bondo Red Cream Hardener Materials Safety Data Sheet, Atlanta, GA, June 2006.
16. Hexion. Hexion 111–1930 Technical Data Sheet, Columbus, OH, May 2005.
17. Fink, J. K. *Reactive Polymers Fundamentals and Applications: A Concise Guide to Industrial Polymers*; William Andrew Publishing: Norwich, New York, 2005.
18. La Scala, J. J.; Palmese, G. R.; Sands, J. M. Composite Repair Resins Containing Minimal Hazardous Air Pollutants and Volatile Organic Compounds. U.S. Patent Appl. 11/689,191, August 2007.
19. Sartomer. Technical Data Sheet for CN151, Exton, PA, May 1999.
20. Bondo Corporation. Bondo Fiberglass Resin Materials Safety Data Sheet, Atlanta, GA, May 2006.
21. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1994.
22. ASTM D 790-92. *Annual Book of ASTM Stand.* **1987**, Vol. 08.01; pp 155–162.
23. Wool, R. P. *Polymer Interfaces, Structure, and Strength*; Hanser Publishers: New York, 1995; pp 102–116.

List of Symbols, Abbreviations, and Acronyms

ARL	U.S. Army Research Laboratory
DMA	dynamic mechanical analysis (polymer thermomechanical analysis)
E'	storage modulus
E''	loss modulus
FAM	fatty acid monomer
FG	fiberglass
HAP	hazardous air pollutant
M	magnesium carbonate, MgCO_3
MFA	methacrylate fatty acid
MLau	methacrylate lauric acid
MOct	methacrylate octanoic acid
MS	glass microspheres
N	sodium metaborate, NaBO_2
NESHAP	National Emissions Standards for Hazardous Air Pollutants
T	talc
$\tan(\delta)$	ratio of loss modulus to storage modulus
T_g	glass transition temperature of polymer
TGA	thermogravimetric analysis
UPE	unsaturated polyester
VE	vinyl ester

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